FINAL REPORT

IOWA HIGHWAY RESEARCH BOARD

RESEARCH PROJECT HR-243

PRODUCTION AND EVALUATION OF CALCIUM MAGNESIUM ACETATE

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TABLE OF CONTENTS

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INTRODUCTION

Calcium magnesium acetate (CMA) has been identified by Bjorksten Research Laboratories as an environmentally harmless alternative to sodium or calcium chloride for deicing highways. Their study found CMA to be noncorrosive to steel, aluminum and zinc with little or no anticipated environmental impact. When used, it degrades into elements found in abundance in nature. The deicing capabilities were found to be similar to sodium chloride. The neutralized CMA they produced did cause scaling of PC concrete, but they did not expect mildly alkaline CMA to have this effect.

In the initial investigation of CMA at the Iowa DOT laboratory, it was found that CMA produced from hydrated lime and acetic acid was a light, fluffy material. It was recognized that a deicer in this form would be difficult to effectively distribute on highways without considerable wind loss. A process was developed to produce CMA in the presence of sand to increase particle weight. In this report the product of this process, which consists of sand particles coated with CMA, is referred to as "CMA deicer". The mixture of salts, calcium magnesium acetate, is referred to as "CMA".

The major problems with CMA for deicing are: (1) it is not commercially available, (2) it is expensive with present production methods and (3) there is very little known about how it performs on highways under actual deicing conditions. In view of the potential benefits this material offers, it is highly desirable to find solutions or answers to these problems. This study provides information to advance that effort.

OBJECTIVES

The study consisted of four principal tasks which were:

1. Production of CMA Deicer

   The objective was to further develop the laboratory process for producing CMA deicer on a pilot plant basis and to produce a sufficient quantity for field trials. The original proposal called for producing 20 tons of CMA deicer.

2. Field Evaluation of CMA Deicer

   The objective was to evaluate the effectiveness of CMA deicer when used under field conditions and obtain information on application procedures. Performance was compared with a regular 50/50 mixture of sand and sodium chloride.

3. Investigation of Effects of CMA on PC Concrete

   The objective was to determine any scaling effect that mildly alkaline CMA might have on PC concrete. Comparison was made with calcium chloride.

4. Determine Feasibility of Producing High Magnesium CMA

   The objective was to investigate the possibility of producing a CMA deicer with a magnesium acetate content well above that produced from dolomitic lime. A high magnesium acetate content is desirable because pure magnesium acetate has a water eutectic of -22 deg. F. as compared with 5 deg. F. for calcium acetate and is therefore a more effective deicer.

PROCEDURES

1. Production of CMA Deicer

   The CMA deicer was first produced in a 6 cu. ft. cement mixer using a mixture of glacial acetic acid, hydrated lime (40% magnesium hydroxide), dry concrete sand, and an agent to promote adhesion of the CMA to the sand particles. Proportions of acid and lime were determined for complete reaction and the ratio of sand to CMA was 3:1. The cement mixer was modified with a lid. Acid was introduced through a spray nozzle using a Tat High-cap pump. Ventilation for the operation was provided by a system for exhausting auto fumes.

A weighed amount of concrete sand was placed in the mixer followed by the coating agent. This mixture was mixed for about 20 minutes prior to addition of the hydrated lime. The lime was mixed in with the sand for an additional 20 minutes. The measured amount of acetic acid was then sprayed into the rotating mixer. Mixing was continued until the outer surface of the mixer began to cool indicating completion of the reaction. The resulting deicer was then removed and stored in 55 gallon drums.

To increase production, a cement mixer of the old pug mill type was modified with a lid, acid spray bar and venting system.

2. Field Use of CMA Deicer

Two test sections of highway were used for field trials. The first was the westbound lane of four-lane U.S. 30 beginning at the Ames maintenance garage and extending westerly to Elwood Drive including the off-ramp at Elwood Drive (about 4 miles). The second was two-lane U.S. 69 from South 16th Street in Ames south to secondary road E-57 (about 3.5 miles). CMA deicer was also used for a frost run on the 3 bridges of the westbound test section on U.S. 30. Locations of these test sections are shown on the map on page 9.

Application of the CMA deicer was made by Ames maintenance garage forces using a hopper spreader calibrated to deliver 300 lbs. per lane mile. The regular sand-salt deicer was applied at the same rate to eastbound U.S. 30 opposite the CMA test section.

3. Scaling of PC Concrete

The scaling effect of CMA on PC concrete was studied by ponding a 5% CMA solution (with a pH of 9) on dished concrete specimens and subjecting them to 100 freeze-thaw cycles.

A 5% solution of calcium chloride was also placed on dished concrete specimens and subjected to freeze-thaw for comparison.

4. High Magnesium CMA

This study involved a literature search for possible natural sources of magnesium carbonate or other high magnesium compounds. The process of separating magnesium carbonate from dolomite was also investigated.

DISCUSSION OF RESULTS

1. Deicer Production

About 10.5 tons of CMA deicer was produced for field trials at a raw material cost of $130 per ton. The production process was generally successful in producing the desired product although there was some minor problems as might be expected with a new product and process.

Equipment for the operation was crude, requiring periodic modification and repair. There was also a problem with the CMA deicer caking on the sides of the mixer. The caked material was easily scraped loose but this was a time consuming hand operation that might have been eliminated by a mixer lined with rubber or some other non-stick surface.

All of the deicer produced contained an excess of acetic acid resulting in an acidic product with a noticable odor. The amount of acid used was reduced on several occasions but never sufficiently to produce an alkaline product. Apparently the acid and lime did not react completely as expected. This indicates that the lime was old and had degraded in part to carbonates which would react slowly. Another possible explanation is encapsulation of unreacted lime with CMA, although evidence of this was not apparent.

The excess acid in the final product was removed by roasting in a ventilated oven at 105 deg. C. The heat caused the CMA layer on some of the sand particles to powder or flake off due to loss of water of hydration. This produced a dusty product with lower than normal deicing capabilities. The CMA dust would easily be blown away or only provide surface melting of ice.

A 5% solution of this dried deicer had a pH of 5.3 and was found to be more corrosive to ferrous metals than a 5% solution of rock salt (sodium chloride). The CMA solution had no effect on aircraft aluminum sheeting while the rock salt solution caused pitting. An aircraft brake drum was badly rusted by both solutions. It was apparent that a CMA deicer must be alkaline to obtain the noncorrosive benefits.

Ventilation for the operation was marginal although adequate to prevent any hazard. Acetic acid fumes have an unpleasant, pungent odor and can irritate mucous membranes. The odor is detectable at concentrations less than 1 ppm and the threshold limit is 10 ppm. The highest concentration measured in the production area was 5 ppm which occurred shortly after an acid spill. The high reading taken during normal operation was 2.5 ppm while most readings were below 1 ppm. An attempt was made to produce the material outside but the twenty degree temperature dissipated the reaction heat too fast.

The 109 deg. F. flash point of glacial acetic acid was also of concern because the temperature generated by the reaction was slightly above 140 deg. F. Precautions were taken to avoid sparks or open flames and no problem was experienced.

2. Field Trials

Six field applications of CMA deicer were made in early April 1982 including one frost run. Highway conditions varied from patches of packed snow to thin ice films and temperatures ranged from 18 to 24 deg. F. Both morning and evening applications were made and sky conditions varied from complete overcast to clear and sunny.

The trials were generally successful with no striking difference between the performance of the CMA deicer and the regular sand-salt mixture. The potential effectiveness of a CMA deicer was not completely realized because of the powdery product being used and because of some application problems. During handling of the deicer and application, the powdered CMA was observed being blown away.

The CMA deicer had a tendency to be applied in small concentrated patches rather than being evenly distributed over the roadway. Regular deicer is thoroughly wet when applied but the CMA deicer was essentially dry. The maintenance workers have observed that wet deicer sticks to the surface more readily than dry deicer and is more evenly distributed from the truck. Although CMA deicer cannot be wetted with water without dissolving the layer of CMA on the sand particles, it can be wetted with a saturated solution of CMA.

Only one frost run was made with CMA deicer. Unfortunately there was no frost on the bridges that morning even though heavy frost was apparent on surrounding surfaces. The CMA deicer did work effectively on the frost present on the bridge approaches.

3. Effect on PC Concrete

The CMA treated concrete specimens showed no scaling after 100 freeze-thaw cycles. This contrasts drastically with the bad scaling that occurred on the calcium chloride treated specimens after 60 freeze-thaw cycles. Apparently an alkaline CMA deicer is necessary to avoid the scaling effect experienced by the Bjorksten Laboratories.

4. High Magnesium CMA

Magnesium carbonate is present in abundance at a Utah deposit, however, the only economic source in Iowa is dolomitic limestone. One interesting source of dolomite is the cement plant quarries in Mason City where dolomite cannot be used for cement production. To obtain a concentration of magnesium above the normal 40%, the calcium carbonate would have to be separated from the dolomite. This separation is possible, but the process is too expensive to make it a viable ingredient in the manufacture of CMA deicer.

5. Related Information

This study has demonstrated that an effective CMA deicer can be produced. Problems uncovered in production and field application were minor and can be solved with relative ease. Environmental impact is expected to be low, however, this aspect is being fully investigated by the California DOT under research sponsored by the Federal Highway Administration. The major problem with CMA deicer is high cost which results from the cost of acetic acid.

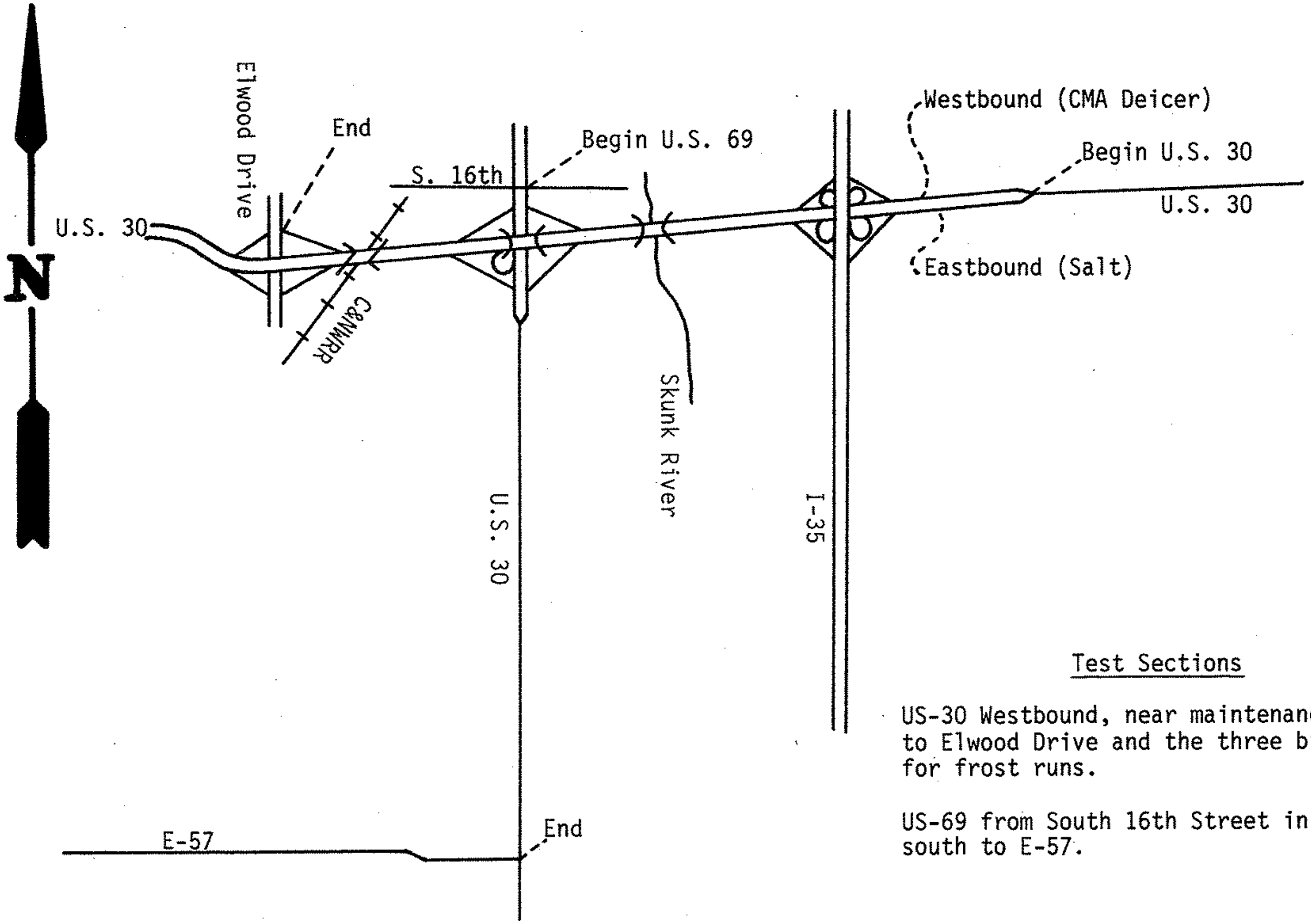
The continuing efforts to develop a process that produces low cost acetic acid have not yet been successful. The enormous potential savings derived from the benefits of CMA deicer would appear to justify a higher cost than rock salt or calcium chloride. In any event, the real breakthrough for CMA deicer will come when lower cost acetic acid becomes available.

CONCLUSIONS

1. CMA deicer as produced by the process developed at the Iowa DOT Materials Laboratory is an effective highway deicer.
2. To obtain all benefits expected from CMA deicer, the product must be alkaline.
3. Alkaline CMA has no scaling effect on PC concrete.
4. CMA deicer with a magnesium content higher than that obtained from dolomitic hydrated lime is not a viable alternate in Iowa.

RECOMMENDATIONS

It is recommended that additional CMA deicer be made for use and development during the full 1982-1983 winter season. It is further recommended that this deicer be made in rented or contracted facilities that are better equipped to produce the product in larger quantities.



<u>Test Sections</u>

US-30 Westbound, near maintenance garage to Elwood Drive and the three bridges for frost runs.

US-69 from South 16th Street in Ames south to E-57.

CMA DEICER TEST LOCATIONS

HR-243